

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-00-

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-01-4302). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 06/10/2000	2. REPORT TYPE FINAL	3. DATES COVERED (From - To) 1996 - 2000
4. TITLE AND SUBTITLE CHROMOPHORES FOR ELECTRO-OPTIC MATERIALS WITH ENHANCED PERFORMANCE		5a. CONTRACT NUMBER F49620-96-1-0387
		5b. GRANT NUMBER F49620-96-1-0387
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) SETH R. MARDER		5d. PROJECT NUMBER
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UNIVERSITY OF ARIZONA DEPARTMENT OF CHEMISTRY TUCSON, AZ 85721		8. PERFORMING ORGANIZATION REPORT NUMBER
		ALSO ORIGINALLY AT CALIFORNIA INSTITUTE OF TECHNOLOGY PASADENA, CA 91125
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 801 North Randolph St, Rm 732 Arlington, VA 22203-1977		10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

13. SUPPLEMENTARY NOTES

New organic chromophores were synthesized to study the effect of variation of the donor, the acceptor, and the structure of the intervening conjugated bridge on the magnitude of the optical nonlinearity and on both their thermal and photochemical stability. Thermogravimetric analysis and differential scanning calorimetry, confirmed previous findings that molecules substituted with diarylamino donors were significantly more stable than dialkylamino donors. Under conditions of photolysis molecules substituted with diarylamino donors were more stable in air than those dialkylamino donors; however, this difference was much smaller when the molecules were photolyzed under a nitrogen atmosphere or in polymer films. Molecules substituted with vinylidic-based acceptors, with a hydrogen atom on the carbon, directly bonded to the conjugated bridge were less stable than those that had a carbon atom at this site. Electrochemical studies demonstrated that the former compounds had irreversible reductions, whereas the latter compounds exhibited reversible reductions. The observed instability of the molecules substituted with hydrogen bearing vinylidic-based acceptors may arise from transiently formed radical anions on the vinyl group that are very unstable. These results should aid in the future design of materials that are thermally and photochemically robust.

15. SUBJECT TERMS

Chromophores, Electro-Optics

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 25	19a. NAME OF RESPONSIBLE PERSON Seth R. Marder
a. REPORT Unclass	b. ABSTRACT Unclass	c. THIS PAGE Unclass			19b. TELEPHONE NUMBER (include area code) 520-574-0456 x 13

Introduction

There is considerable interest in electro-optic materials due to the potential for applications of these materials in photonic information technology.¹⁻³ One promising approach toward electro-optic materials involves poled polymers containing nonlinear optical (NLO) chromophores. Significant progress has been achieved towards the design of materials with high optical nonlinearities.⁴ However, device applications of poled polymers require the materials to be stable during device processing. These requirements dictate that the NLO chromophores themselves must have high thermal and photochemical stability during operations for long periods of time. To achieve long-term stability of the electric field induced alignment, high performance polymers, with T_g 's over 200°C, are typically employed. Therefore it is imperative that the NLO chromophores exhibit high thermal stability well over 200°C for times involved in poling, as well as other processing steps.^{5,6}

Chromophores should also be photochemically stable, since the poled polymers will be exposed to high laser intensity in the wavelength range of 800-1550 nm in many applications. Upon exposure to high intensity light at these operating wavelengths, the chromophores could undergo two- or multi-photon absorption processes.⁷ In dipolar chromophores, such processes can populate the lowest singlet excited state, which can also be reached by linear UV-visible absorption processes, where there can be pathways available for photochemical degradation.⁸⁻¹⁰ The mechanism of photochemical degradation of chromophores depends on many factors and is sensitive to the functional groups in the chromophores and the surrounding environment. For example, it has been established that one of the major pathways for photodecomposition of azo dyes involves the photoreduction of the azo moiety.¹¹ The most commonly used donor moieties in donor-acceptor NLO chromophores are based on amino groups. It has been experimentally demonstrated that chromophores bearing dialkylamino groups exhibit low light fastness.¹² This observation has been attributed to an oxygen related degradation process that involves the

abstraction of the hydrogen atoms α - to the nitrogen and generation of reactive radicals.¹³ Therefore, chromophores which lack α -hydrogens have potential for improved light fastness.

Here, we report studies of the thermal and photochemical stabilities of aminostyryl thiophene based donor-acceptor NLO chromophores. The acceptor unit constitutes a tricyanovinyl, dicyanovinyl, β -substituted dicyanovinyl or the heterocyclic phenylisoxazolone acceptor.¹⁴ We compare the stabilities of the chromophores with dialkylamino and diarylamino donor substituents.¹⁵ The effect of structural variation of the acceptor part of the chromophore upon the thermal and photochemical stabilities is also reported. From the electrochemical studies, it is also proposed that the photochemical stability of the chromophores can be correlated to the chemical stability of the radical anions of the chromophores. The structures of the chromophores under study are shown in Figure 1.¹⁶ It is expected that the alkyl and aryl substituents on the chromophores reported here also should enhance the miscibility with the polymer host and reduce chromophore aggregation.¹⁷

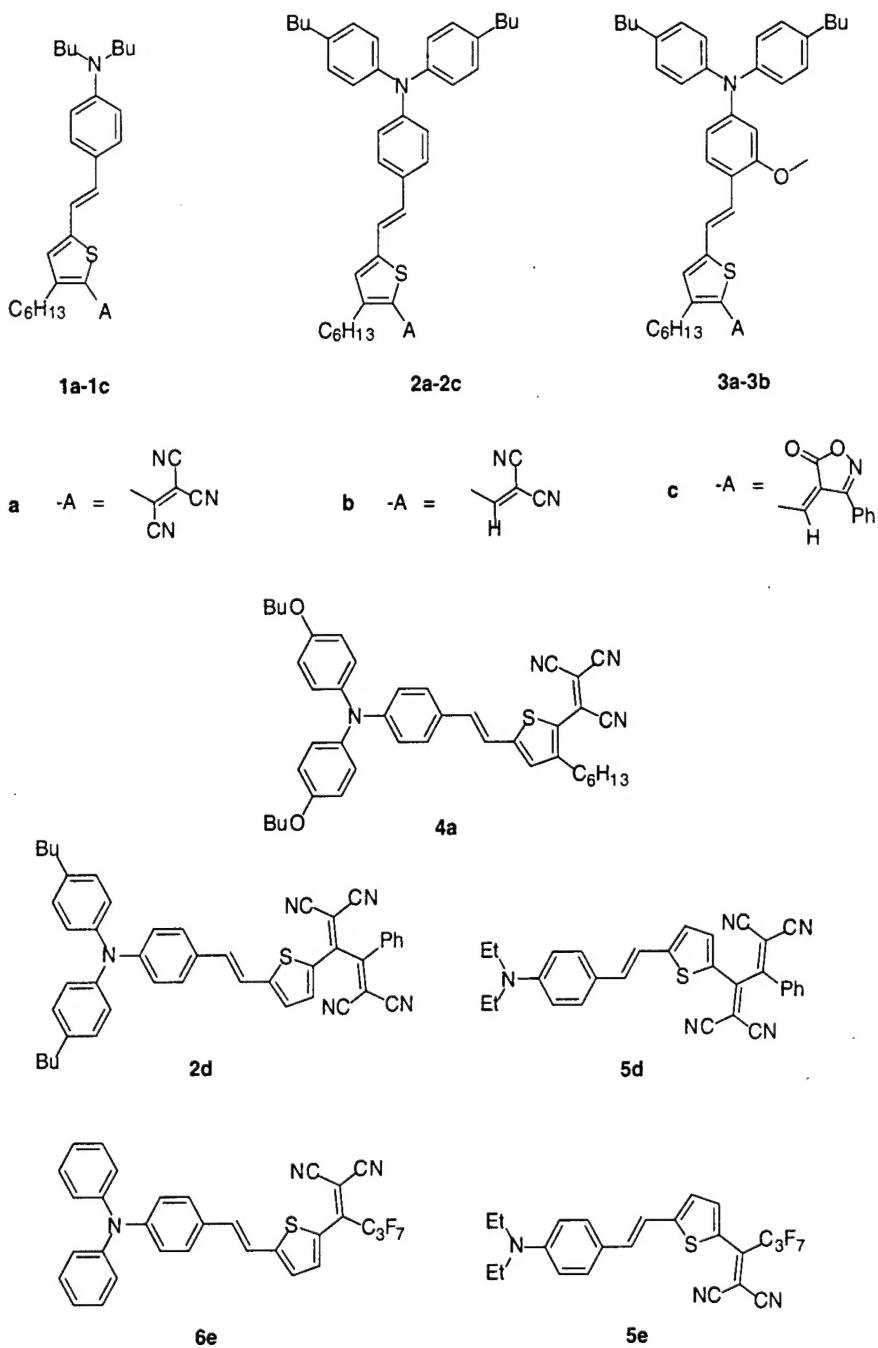


Figure 1. Structures and the Number Scheme for the Chromophores in this Study

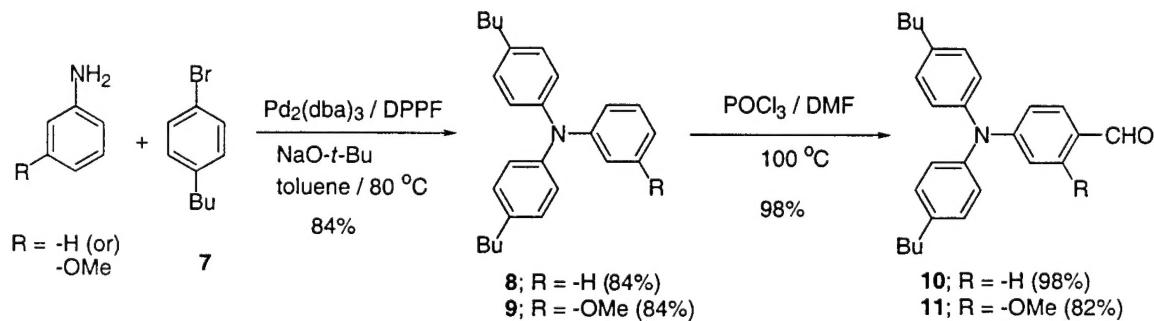
Results

Synthesis

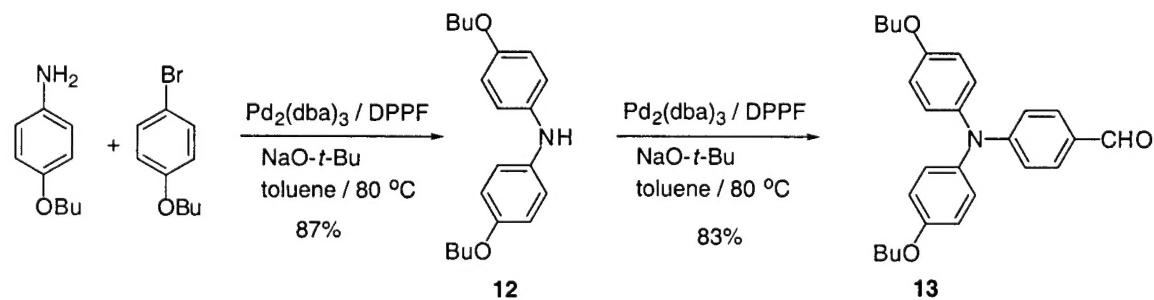
We approached the syntheses of these chromophores in a convergent fashion. The donor triarylamine was synthesized as an aldehyde and the thiophene spacer was synthesized as a

phosphonium salt. The main skeleton of the chromophore was then assembled together by a Wittig reaction. The acceptor group was installed in the last step of the synthesis.

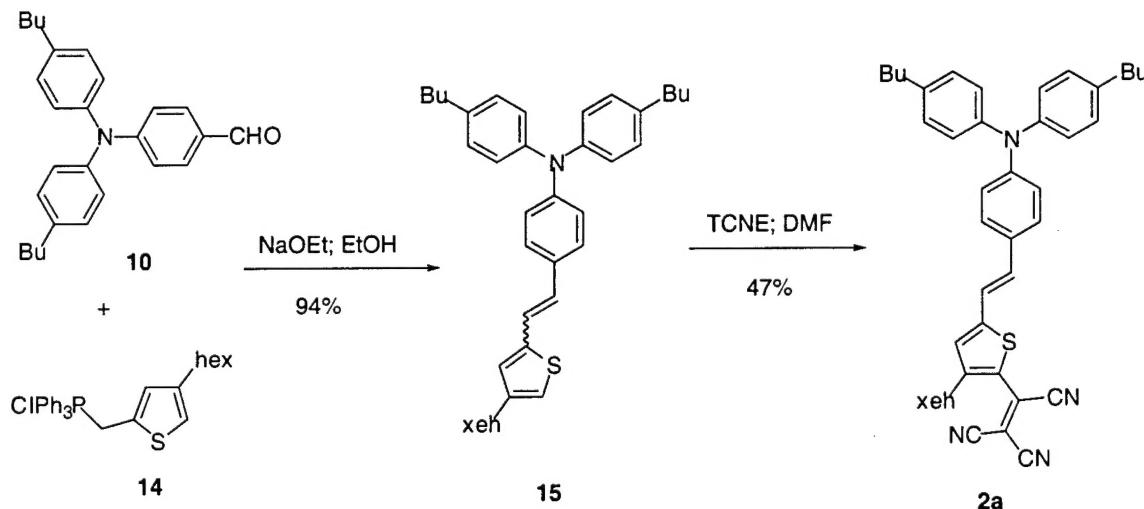
The triarylamine was synthesized using the palladium catalyzed aryl carbon-nitrogen bond forming reaction recently reported in the literature.¹⁹⁻²⁰ Treatment of aniline or *m*-anisidine with 2.2 equivalents of 4-butyl-1-bromobenzene (**7**) in the presence of 1.5 mol% of tris(dibenzylideneacetone)dipalladium and 2.25 mol% of bis(diphenylphosphino) ferrocene (DPPF) afforded 4,4'-dibutyltriarylamine in good yields. The triarylamine was then subjected to Vilsmeir-type reaction conditions to afford the (*p,p'*-dibutyl)diphenylaminoaryl-4-carboxaldehydes **10** and **11**.



The synthesis of 4-(*p,p'*-dibutoxy)diphenylaminobenzaldehyde (**13**) was approached in a stepwise fashion. Treatment of 4-butoxyaniline with 4-bromo-butoxybenzene under palladium catalysis conditions resulted in dibutoxydiphenylamine (**12**) in 87% yield. Treatment of **12** with 4-bromobenzaldehyde under similar conditions afforded the carboxaldehyde **13** in 83% yield.

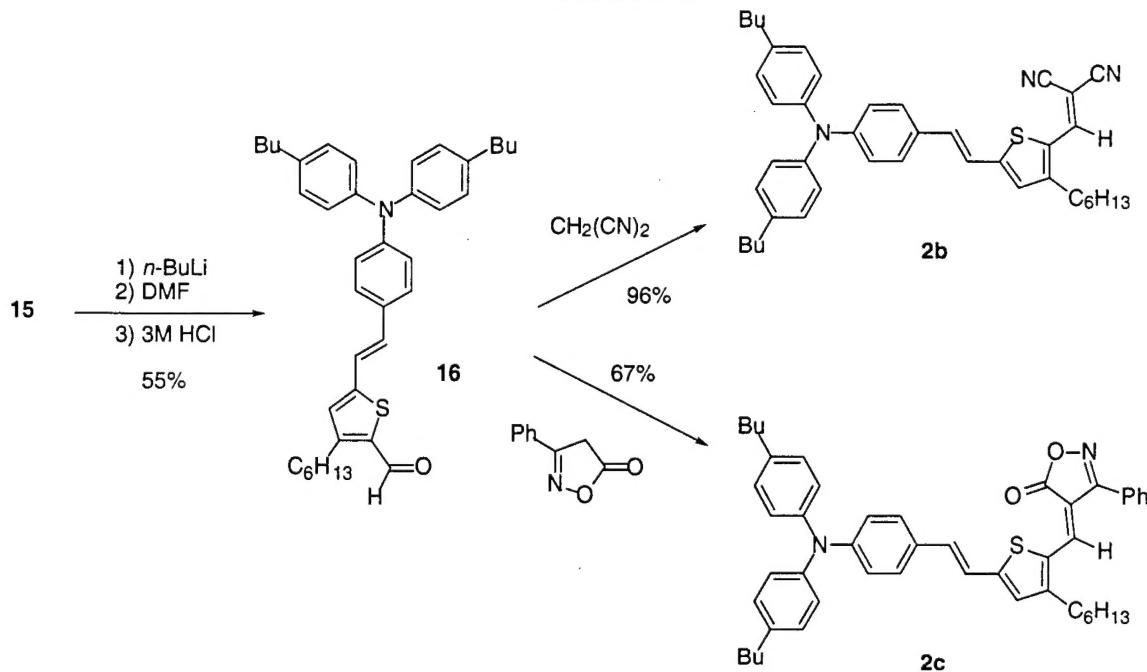


The synthesis of 4-hexylthiophene-2-methylenetriphenylphosphonium chloride (**14**) was previously reported.²⁰ Reaction of **10** with **14** under Wittig reaction conditions using sodium ethoxide as the base afforded the product **15** as a mixture of the *cis*- and *trans*- isomers. Treatment of this mixture with tetracyanoethylene (TCNE) in DMF at 50°C afforded the chromophore **2a** with the tricyanovinyl group as the acceptor in 47% yield. The chromophore **2a** had only the *trans* product. The charge transfer structure for the compound **2a** should have a single bond in place of the double bond in the neutral structure. The tricyanovinyl group, being a strong acceptor, should have significant contribution from the charge transfer form of the structure, thus providing an opportunity for compound **2a** to isomerize to the thermodynamically favorable *trans* isomer.²⁰

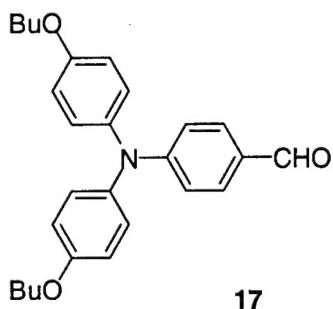
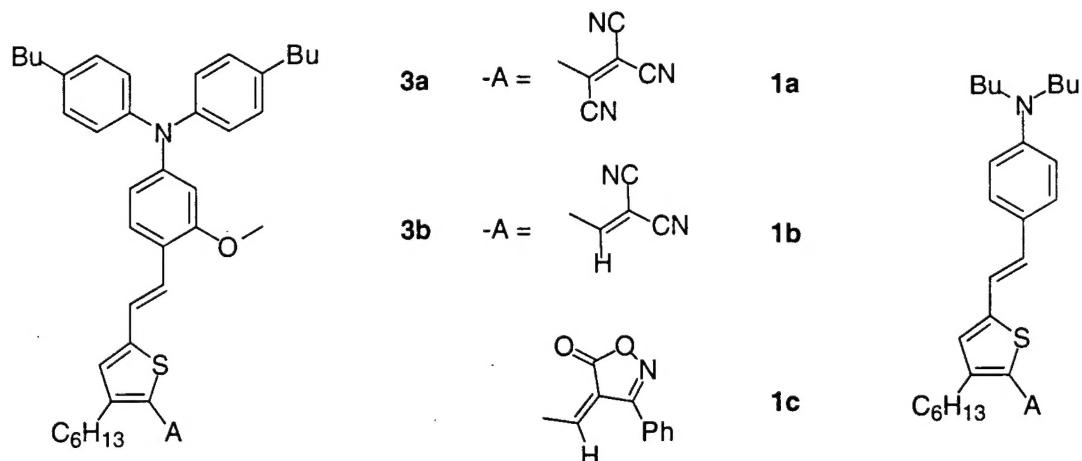


The chromophores **2b** and **2c** with dicyanovinyl and phenylisoxazolone as the acceptors were also synthesized. For this purpose, we synthesized the aldehyde **16** from **15** by deprotonating the thiophene and treating the resultant organolithium intermediate with DMF. The compound **16** was obtained as a 6:4 mixture of *trans* and *cis* isomers. Treatment of this mixture with 3M aqueous hydrochloric acid in THF improved the composition to a ~20:1 mixture as estimated by ¹H NMR. Subjecting the aldehyde Knovenagel condensation with malononitrile and 3-phenylisoxazolone afforded the chromophores **2b** and **2c** respectively as shown in Scheme 1. The *trans* isomer of the chromophores was isolated as the only characterizable products.

Scheme 1



The methoxy substituted chromophores **3a** and **3b** were synthesized through the same route by using **11** in the place of **10**. Similarly the chromophores **1a-1c** were synthesized through the same route by using the commercially available 4-(*N,N*-dibutylamino)benzaldehyde in the place of **10**. Chromophore **4a** was synthesized using **17** as the precursor.

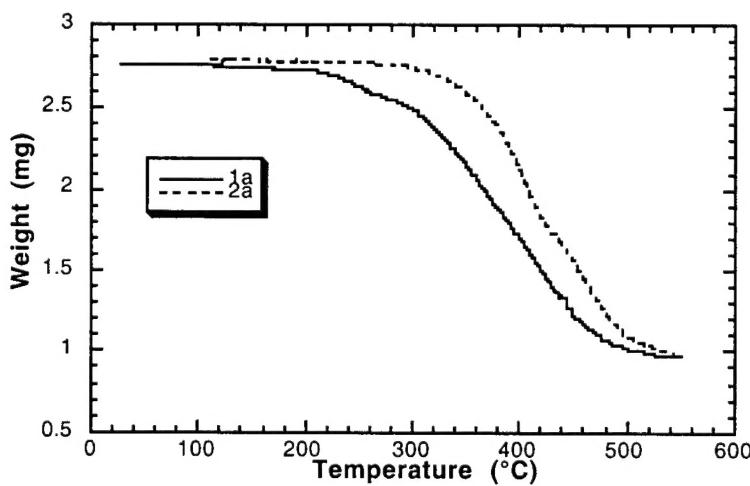


Thermal Stability

Chromophores with diarylamino groups as donor moieties exhibit enhanced thermal stabilities compared to their counterparts with dialkylamino moieties (compare entries 1 vs. 2 and 5 vs. 6 in Table I). The magnitude of the stability enhancement depends on the acceptor moiety. The tricyanovinyl substituted chromophore **1b** exhibits a stability enhancement of about 140°C compared to **1a** (see Figure 2), while the enhancement from **2a** to **2b** was only about 60°C. There is no significant difference in the stability of the chromophores **1c-3c** with phenylisoxazolone acceptor.

Table I: Thermal Decomposition of the NLO Chromophores

Entry	Compound	R ₂ N-	Acceptor	T _d (°C)
1	1a	Bu ₂ N-	-(CN)C=C(CN) ₂	204
2	2a	Ar ₂ N-	-(CN)C=C(CN) ₂	344
3	3a	Ar ₂ N-Ar'(OMe)-	-(CN)C=C(CN) ₂	325
4	4a	(BuO-Ar) ₂ N-	-(CN)C=C(CN) ₂	351
5	1b	Bu ₂ N-	-CH=C(CN) ₂	321
6	2b	(Bu-Ar) ₂ N-	-CH=C(CN) ₂	383
7	3b	Ar ₂ N-Ar'(OMe)-	-CH=C(CN) ₂	375
8	1c	Bu ₂ N-	-CH=isox	233
9	2c	(Bu-Ar) ₂ N-	-CH=isox	242
10	3c	Ar ₂ N-Ar'(OMe)-	-CH=isox	232

**Figure 2.** Thermogravimetric analysis of **1a** and **2a**.

Chromophores with phenylisoxazolone acceptor group decompose at around 230°C independent of other functionalities. At this temperature there is a small yet significant loss of

weight. When the chromophore **1c** is heated at 250°C for 20 minutes, the peak corresponding to the C=O stretching at 1743 cm⁻¹ disappeared in the IR spectrum.²¹

Recently, we have reported the syntheses of chromophores functionalized with hydroxy groups to facilitate covalent incorporation on to high performance polymers.²⁰ Covalent incorporation of these chromophores on to polymers functionalized with phenolic groups results in additional ethereal linkages in the materials. Therefore, a study on the effect of ethereal linkages upon thermal stability is interesting. In addition to potentially higher optical nonlinearities due to the enhanced donor strength in the chromophores **3a-c** and **4c**, they also have additional ethereal functionalities compared to **2a-c** to facilitate a study on their effect upon thermal stability. The chromophores **3a** and **4a**, with a methoxy group and two butoxy groups respectively, exhibit thermal stabilities that are similar to the chromophore **2a**.

Photochemical Stability

The B-values and the relative rates of decomposition of the chromophores in toluene upon irradiation for 1 hour at 350 nm are listed in Table II. It is clear that the behavior of the chromophores depend on the donor moiety. Compounds with the diarylamino donors decompose much more slowly than the corresponding dialkylamino donor based chromophores (for example, compare **1a** with **2a**). The magnitude of enhancement of photostability of the chromophore is coupled to the nature of the acceptor moiety. Replacing a dialkylamino donor substituent with a diarylamino donor substituent in a tricyanovinyl based chromophore results in a large increase in photostability, while such a modification in the phenylisoxazolone based chromophore results in a smaller enhancement (compare entries **1a** vs. **2a** and **1c** vs. **2c** in Table II). Increasing the donor strength through installation of an additional methoxy group or two butoxy groups results in the deterioration of the photostability of the chromophore (compare **2a**, **3a** and **4a** in Table II).

Upon irradiating a solution of **1b** and **2b** with 350 nm light, the absorbance at the λ_{max} of the UV-visible spectra fluctuated up and down within about 15% of its original value. To test the possibility of *trans-cis* isomerization as the reason for such an observation, solutions of **1b** were

irradiated for 15 minutes and 60 minutes and ^1H NMR of these samples were acquired. The chromophore remained as a purely trans isomer in either of these samples within the experimental error of ^1H NMR. Also, there were no other identifiable impurities by ^1H NMR spectra. At this time, the origin of the fluctuations in the absorbance is not clear.

Table II: Photochemical Decomposition of NLO Chromophore Solutions in Toluene after Irradiation at 350 nm.

	$\text{R}_2\text{N}-$	Acceptor	B-value ($\times 10^4$) photons / molecule	Decomposition rate constant ^{b)} ($\times 10^{-5}$) min^{-1} (with oxygen)	Decomposition rate constant ^{b)} ($\times 10^{-5}$) min^{-1} (deoxygenated)
1a	$\text{Bu}_2\text{N}-$	$-(\text{CN})\text{C}=\text{C}(\text{CN})_2$	5.26	56	27
2a	$\text{Ar}_2\text{N}-$	$-(\text{CN})\text{C}=\text{C}(\text{CN})_2$	18.50 ^a	7	11
3a	$\text{Ar}_2\text{N}-\text{Ar}'(\text{OMe})-$	$-(\text{CN})\text{C}=\text{C}(\text{CN})_2$	11.00	17	22
4a	$(\text{BuO}-\text{Ar})_2\text{N}-$	$-(\text{CN})\text{C}=\text{C}(\text{CN})_2$	8.49	17	26
1c	$\text{Bu}_2\text{N}-$	$-\text{CH}=\text{isox}$	5.17	53	55
2c	$(\text{Bu}-\text{Ar})_2\text{N}-$	$-\text{CH}=\text{isox}$	7.70	25	30
5d	$\text{Et}_2\text{N}-$	$-\text{TCBD}$	5.45	27	-
2d	$\text{Ar}_2\text{N}-$	$-\text{TCBD}$	8.63	22	-
5e	$\text{Et}_2\text{N}-$	$-(\text{C}_3\text{F}_7)\text{C}=\text{C}(\text{CN})_2$	5.27	60	28
6e	$\text{Ph}_2\text{N}-$	$-(\text{C}_3\text{F}_7)\text{C}=\text{C}(\text{CN})_2$	8.96	14	21

a) 'B' value reported for the same compound by pump-probe experiment was 3×10^6 (ref 15),

b) the decomposition rate constant is obtained from the slope of the plot of time of irradiation vs.

log (absorbance) at λ_{max} . Uncertainty in decomposition rate constant is estimated to be $\pm 25\%$.

We noticed that the dicyanovinyl based chromophores do not exhibit fluctuations in the UV-visible absorbance, when irradiated after incorporation into a polymer host as a thin film. Therefore, the photochemical decomposition trend of **1b** and **2b** compared to other chromophores should be clear in the study of thin films. The chromophores were spin-coated on to glass slides with PMMA as the polymer host and chlorobenzene as the solvent. The relative rates of decomposition of the chromophores are shown in Table III. In all the cases, the chromophores

containing the diarylamino donors exhibited much higher photostabilities than the corresponding chromophores with dialkylamino donors. The decomposition rate of the chromophores also depended on the acceptor. The chromophores with the tricyanovinyl group as the acceptor were the most stable among the acceptors studied. The photostability of the chromophores based on the phenylisoxazolone group acceptor exhibited better stabilities than the chromophores based on dicyanovinyl group, but both of these were worse than the tricyanovinyl based compounds. The chromophores **2d** and **5d** with a tetracyanobutadiene (TCBD) acceptor moiety exhibited better stabilities than the phenylisoxazolone chromophores in solution. It is also noted that the chromophores **5e** and **6e** with the heptafluoropropyl group as the β -substituent in the acceptor moiety exhibited better photostability than the dicyanovinyl chromophores **1b** and **2b** in thin film studies. The overall trends in stabilities of chromophores are similar in both thin film studies and solution studies, even though the magnitudes of stabilities are different.

Table III: Photochemical Decomposition of NLO Chromophore in thin film after Irradiation at 350 nm.

Compound	R ₂ N-	Acceptor	Relative rate ^{a)} (x 10 ⁻⁵ min ⁻¹)
1a	Bu ₂ N-	-(CN)C=C(CN) ₂	18
2a	Ar ₂ N-	-(CN)C=C(CN) ₂	9
1b	Bu ₂ N-	-HC=C(CN) ₂	15
2b	Ar ₂ N-	-HC=C(CN) ₂	78
1c	Bu ₂ N-	-CH=isox	65
2c	(Bu-Ar) ₂ N-	-CH=isox	46
5e	Et ₂ N-	-(C ₃ F ₇)C=C(CN) ₂	58
6e	Ph ₂ N-	-(C ₃ F ₇)C=C(CN) ₂	16

a) the decomposition rate constant is obtained from the slope of the plot of time of irradiation vs. log (absorbance) at λ_{max} . Uncertainty in decomposition rate constant is estimated to be $\pm 25\%$.

We hypothesized that the difference in stability between the dialkylamino and diarylamino donors can be ascribed to the relative susceptibilities of these chromophores to photooxidation by oxygen. To test this pathway, the toluene solutions were bubbled with nitrogen for an hour to exclude oxygen.²² Irradiation of these solutions at 350 nm showed a significant enhancement in the photostability of the dialkylamino based tricyanovinyl chromophore **2a**, while it lead to an enhanced stability for the diarylamino chromophore **1a** as shown in Figure 3.^{23,24} In fact, from the results in Table II it can be seen that if anything the diarylamino substituted compounds with tricyanovinyl have a slightly *larger* rate constant for decomposition *under* nitrogen. While in each case the differences in rate are only slightly greater than the error bar for the measurement, the fact that the trend holds for several compounds suggests that the effect is real.

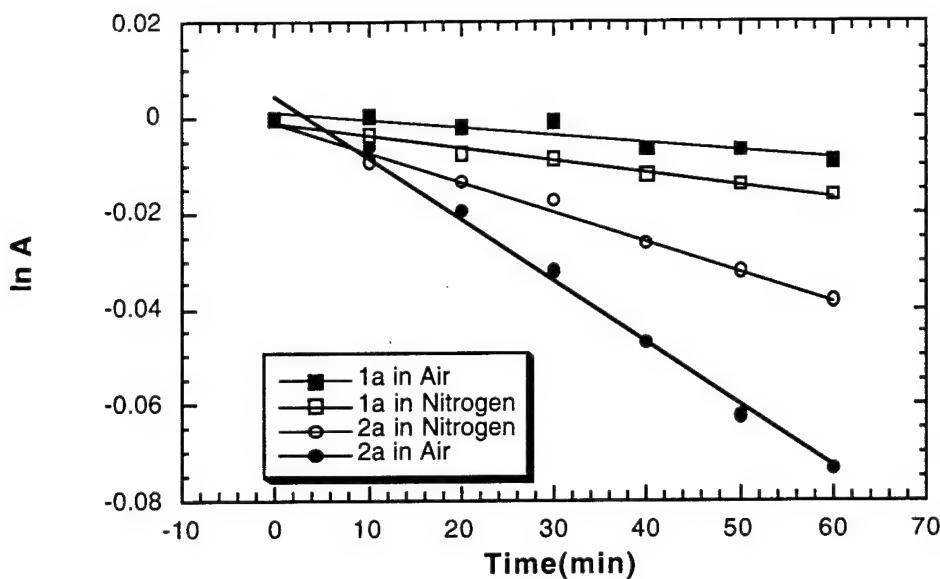


Figure 3. Plot of $\ln(\text{Absorbance})$ versus irradiation time for **1a** in air (filled squares) under nitrogen (open squares); for **2a** in air (filled circles) under nitrogen (open circles).

Electrochemistry

We hypothesized that the potential and the reversibility of oxidation and reduction of the chromophores should provide useful information regarding the photostability of the chromophores. Therefore, a study on the electrochemical behavior of the chromophores should be interesting.

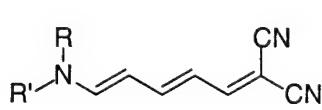
All the chromophores reported in Table IV have reversible oxidations independent of the donor or the acceptor group. However, the reversibility of the reduction wave was found to depend on the acceptor. The reduction of the chromophores **1a-4a** with tricyanovinyl acceptor group are fully reversible, while the reduction of the other chromophores with dicyanovinyl and phenylisoxazolone acceptor moieties are irreversible. It is interesting to note that the chromophores that do not display reversible reduction potentials, such as **1b-3b**, **1c** and **2c**, have a vinyl hydrogen in the acceptor moiety. Also, the chromophores which do have reversible reduction waves lack the vinyl β -hydrogen in the acceptor moiety. For example, the NLO chromophores with dicyanovinyl moiety as the acceptor group **2d**, **5d**, **5e**, and **6e**, all of which have a

substitution at the β -position, exhibit fully reversible reduction waves. Also, it was noted that the chromophore **19** which has a substituent at the β -position exhibits reversible reduction characteristics, while the corresponding chromophore **18** with hydrogen as the substituent exhibits irreversible reduction.²⁵

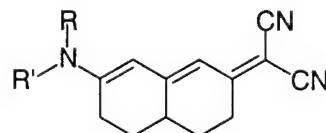
Table IV: Cyclic Voltammetry Data

	Donor	Acceptor	$E_{1/2} [m^+/m^-]$ (mV) ^a	$E_{1/2} [m/m^-]$ (mV)
1a	Bu ₂ N-	-(CN)C=C(CN) ₂	321	-992
2a	Ar ₂ N-	-(CN)C=C(CN) ₂	408	-948
3a	Ar ₂ N-	-(CN)C=C(CN) ₂	367	-960
4a	Ar'(OMe)- (BuO-Ar) ₂ N-	-(CN)C=C(CN) ₂	264	-955
1b	Bu ₂ N-	-CH=C(CN) ₂	268	-1594 ^b
2b	(Bu-Ar) ₂ N-	-CH=C(CN) ₂	370	-1573 ^b
3b	Ar ₂ N-	-CH=C(CN) ₂	327	-1533 ^b
1c	Ar'(OMe)- Bu ₂ N-	-CH=iso _x	242	-1461 ^b
2c	(Bu-Ar) ₂ N-	-CH=iso _x	359	-1444 ^b
3c	Ar ₂ N-	-CH=iso _x	314	-1353 ^b
5d	Ar'(OMe)- Bu ₂ N-	TCBD	322	-847, -1119
2d	Ar ₂ N-	TCBD	399	-822, -1095
5e	Bu ₂ N-	-(C ₃ F ₇)C=C(CN) ₂	291	-1087
6e	Ar ₂ N-	-(C ₃ F ₇)C=C(CN) ₂	495	-1037

a) $E_{1/2}$ relative to Fc^+/Fc in CH_2Cl_2 (0.1M (*n*-Bu₄N⁺)(PF₆⁻)). b) Maximum of the reduction peak is reported. The overall process is not reversible.



18



19

The oxidation potentials are sensitive to the nature of the donor functionality. The chromophores bearing the dilakylamino groups were oxidized at lower potentials than the corresponding bis(butylphenyl)amino moiety by 87-117 mV. The magnitude of the difference in the oxidation potential is dependent on the strength of the acceptor. Such an observation attests the effective communication between the donor and the acceptor moieties through the conjugated π -system. It is interesting to note that the chromophores with phenylisoxazolone moiety are easier to oxidize compared to their counterparts with dicyanovinyl group as acceptor, although the charge transfer band in the linear optical spectra is more red shifted for the chromophores with phenylisoxazolone acceptors. This result is taken to suggest that the substitution of the phenylisoxazolone acceptor in the place of the dicyanovinyl acceptor not only stabilizes the LUMO, it also destabilizes the HOMO level of these chromophores.

It is noteworthy that the presence of additional alkoxy groups in the diarylamino based chromophores affects the oxidation potential of the chromophore. The introduction of a methoxy group on the conjugated bridge renders the chromophores easier to oxidize (for example, compare compounds **2** and the corresponding **3**). These chromophores however, still remain difficult to oxidize when compared to the dialkylamino based chromophores (compare compounds **3** and the corresponding **1**). Introduction of two butoxy groups on the terminal aryl rings instead of the methoxy group in the conjugated bridge has similar effect on the linear optical spectra. However, such a modification renders the chromophore **4a** much easier to oxidize than even the dialkylamino based chromophore **1a**.

Discussion

Chromophores with diarylamino groups as donor moieties exhibit enhanced thermal stabilities compared to their counterparts with dialkylamino moieties, consistent with previous observations.⁵ It is noteworthy that the magnitude of the enhancement in stability upon diarylamino substitution is coupled to the nature of the acceptor moiety. It is reasonable to assume that the difference in the magnitude depends on the relative contribution of the acceptor moiety in the overall thermal decomposition process. For example, the chromophores with

phenylisoxazolone acceptor **1c-3c** do not exhibit any significant difference in thermal stabilities, since the major pathway for the thermal degradation involves the acceptor moiety. The mechanism of decomposition presumably involves the decomposition of these chromophores through loss of CO₂ in the acceptor moiety, occurs at around 230°C.²⁶ The onset of thermal decomposition of the chromophores clearly showed a dependence on the acceptor moiety. The chromophores with dicyanovinyl group are stable at temperatures over 300°C (entries 5-7 in Table I), while the corresponding chromophores with tricyanovinyl moiety are relatively less stable (entries 1-4 in Table I).

Substitution of two butoxy groups in the place of butyl groups on the donor part of the chromophore did not have any deleterious effect on the thermal stability of the chromophores (compare **2a** with **4a** in Table I). Similarly, the installation of an additional methoxy group on the conjugated bridge did not have any significant effect on the thermal stability of the chromophores (compare **2a** with **3a** and **2b** with **3b** in Table I). These results suggest that unfunctionalized chromophores can be used as model compounds to study the thermal stabilities of functionalized chromophores with ether functionalities upon attachment to functionalized polymers.

The photochemical decomposition of organic chromophores with dialkylamino moieties could involve the formation of a radical cation on the amino donor through photooxidation and subsequent α -hydrogen abstraction.²⁷ We therefore hypothesized that replacing the alkyl groups with aryl groups in the donor part of the chromophore should increase the oxidation potential and also obviate the above decomposition mechanism due to the absence of hydrogen atoms α - to the nitrogen. It is clear from the results listed in Table II that the compounds with the diarylamino donors decompose much more slowly than the corresponding dialkylamino donor based chromophores. Since the mechanism of the α -hydrogen abstraction involves oxygen, the enhancement in photostability upon bubbling with nitrogen is more pronounced with dialkylamino based chromophores (see Figure 3). Increasing the donor strength through installation of an additional methoxy group or two butoxy groups results in the deterioration of the photostability of the chromophore (compare entries 2, 3 and 4 in Table II). It is noteworthy, however, that

precluding hydrogens α - to the nitrogen did not completely obviate the degradation process of the diarylamino based chromophores. This result is taken to suggest that additional decomposition pathways operate in the photochemical degradation of the chromophores.

The magnitude of enhancement in photostability, upon replacing a dialkylamino group with a diarylamino moiety, is coupled to the nature of the acceptor group. Replacing a dialkylamino moiety with a diarylamino moiety in a tricyanovinyl based chromophore results in a large increase in photostability, while such a modification in the phenylisoxazolone based chromophore results in a much smaller enhancement of photostability (compare entries **1** vs. **2** and **5** vs. **6** in Table II). The difference in the magnitude of stability enhancement is attributed to the decomposition pathways available through the acceptor moiety. If the acceptor moiety provides a facile pathway for degradation, then the differences in stability between the diarylamino and dialkylamino based chromophores are small. However, if the acceptor moiety is relatively photostable, then the differences between the dialkylamino and diarylamino chromophores become larger, since the relative oxidative stability of the donor moieties dictates the relative overall stability of the chromophore.

It was also observed that the substituent at the β -position of the vinyl group significantly influences the stability of the chromophore. For example, the stability difference between **1b** and **2b** is smaller when compared to the stability difference between **5e** and **6e**. This observation suggests that the acceptor moiety with the heptafluoropropyl substituent stabilizes the dicyanovinyl based acceptor unit. This effect is attributed to the chemical stability differences between the radical anions of the acceptors as observed in electrochemical studies. We suggest that radical anions can be formed in these chromophores upon irradiation through a photoinduced electron transfer from the amino donor to the acceptor moiety.²⁸ It should be noted that, despite the presence of a β -substituent, the difference between the stability of the chromophores **2d** and **5d** is small. We suggest that the presence of butadiene moiety in the acceptor moiety renders the chromophore susceptible to Diels-Alder type pathway for decomposition through inverse electron demand.²⁴ Finally, the fact that the diarylamino substituted compounds with the tricyano vinyl

acceptor may decompose photolytically slightly *faster under* nitrogen than in air, suggests that this effect should be examined further for other systems containing very strong acceptors and has implications for packaging strategies. In particular, it may bring into question, the need to take drastic steps to exclude all oxygen.

Summary

Thermal and photochemical stabilities of several NLO chromophores have been studied. Diarylamino donor based chromophores exhibit enhanced thermal stabilities compared to their dialkylamino counterparts. The magnitude of the enhancement is coupled to the stability of the acceptor moiety. The photostabilities of the chromophores are correlated to the chemical stabilities of the radical cations and radical anions. The differences in photostability between the dialkylamino and diarylamino moieties are attributed to the differences in the radical cation stability of the chromophore. The radical cations of the dialkylamino moieties can undergo facile decomposition through the α -hydrogen, while with diarylamino moieties this pathway is not available. Similarly the chromophores with chemically stable radical anions, as estimated by their electrochemical behavior, exhibited better photostabilities. Thus, we suggest the presence of substituents in the acceptor moiety that stabilizes the chemical stability of the radical anion will provide enhanced photostabilities.

References

- 1) (a) Nonlinear Optical Properties of Organic Molecules and Crystals; Chemla, D.S.; Zyss, J. Eds.; Academic Press; New York, 1987. (b) Materials for Nonlinear Optics: Chemical Perspectives; Marder, S.R.; Sohn, J.E.; Stucky, G.D. Eds.; *ACS Symposium Series*, **1991**. (c) Optical Nonlinearities in Chemistry; special issue of *Chem. Rev.* **1994**, 94, issue no. 1. (d) Marder, S.R.; Perry, J.W. *Science*, **1993**, 263, 1706. (e) Miyata, S.; Sasabe, H. *Poled Polymers and Their Applications to SHG and EO Devices*, Gordon and Breach, Amsterdam, 1997. (f) Kajzar, F.; Swalen, J. *Organic Thin Films for Waveguiding Nonlinear Optics*, Gordon & Breach, Amsterdam, 1996. (g) Nalwa, H.S. *Nonlinear Optics of Organic Molecules and*

Polymers, CRC Press, Boca Raton, 1997. (h) Kuzyk, M.G.; Singer, K.D.; Twieg, R.J. *J. Opt. Soc. Am. B. Opt. Phys.* **1998**, *15*, 254.

2) For a recent review, see: (a) Marder, S.R.; Kippelen, B.; Jen, A.K.-Y.; Peyghambarian, N. *Nature*, **1997**, 845. (b) Wolff, J.J.; Wortmann, R. *J. Prakt. Chem.* **1998**, *340*, 99. (c) Denning, R.G. *J. Mater. Chem.* **1995**, *5*, 365.

3) (a) Shi, Y.; Steier, W.H. *Appl. Phys. Lett.* **1991**, *59*, 2935. (b) Diemeer, M.B.J.; Suyten, F.M.M.; Trommel, E.S.; McDonahc, A.; Copeland, J.M.; Jennekens, L.W.; Horsthuis, W.H.G. *Electr. Lett.* **1990**, *26*, 379. (c) Ivanov, M.; Todorov, T.; Nikolova, L.; Tomova, N.; Dragostinova, V. *Appl. Phys. Lett.* **1995**, *66*, 2174. (d) Kippelen, B.; Meyers, F.; Peyghambarian, N.; Marder, S.R. *J. Am. Chem. Soc.* **1997**, *119*, 4559.

4) For examples of second-order nonlinear optical chromophores with high $\mu\beta$, see: (a) He, M.; Zhu, J.; Harper, A.W.; Sun, S.-S.; Dalton, L.R.; Garner, S.M.; Chen, A.; Steier, W.H. *ACS Symposium Series*, **1997**, *695*, 258. (b) Ahlheim, M.; Barzoukas, M.; Bedworth, P.V.; Blanchard-Desce, M.; Fort, A.; Hu, Z.-Y.; Marder, S.R.; Perry, J.W.; Runser, C.; Staehelin, M.; Zysset, B. *Science*, **1996**, *271*, 335. (c) Blanchard-Desce, M.; Alain, V.; Bedworth, P.V.; Marder, S.R.; Fort, A.; Runser, C.; Barzoukas, M.; Lebus, S.; Wortmann, R. *Chem. Eur. J.* **1997**, *3*, 1091.

5) (a) Moylan, C.R.; Twieg, R.J.; Lee, V.Y.; Swanson, S.A.; Betterton, K.M.; Miller, R.D. *J. Am. Chem. Soc.* **1993**, *115*, 12599. (b) Twieg, R.J.; Burland, D.M.; Hedrick, J.; Lee, V.Y.; Miller, R.D.; Moylan, C.R.; Seymour, C.M.; Volkson, C.A.; Walsh, C.A. *Proc. SPIE*, **1994**, *2*, 2143.

6) (a) Jen, A.K.-Y.; Cai, Y.; Bedworth, P.V.; Marder, S.R. *Adv. Mater.* **1997**, *9*, 132. (b) Bedworth, P.V.; Cai, Y.; Jen, A.; Marder, S.R. *J. Org. Chem.* **1996**, *61*, 2242.

7) For a review on two-photon processes, see: Birge, R.R. *Acc. Chem. Res.* **1986**, *19*, 138.

8) For an illustration of the possible photophysical and photochemical pathways of an excited chromophore, see: Suratwala, T.; Gardlund, Z.; Davidson, K.; Uhlmann, D.R.; Watson, J.; Bonilla, S.; Peyghambarian, N. *Chem. Mater.* **1998**, *10*, 199.

9) For studies on decomposition of chromophores through multi-photon processes, see: (a) Motazavi, M.A.; Yoon, H.N.; Teng, C.C. *J. Appl. Phys.* **1993**, *74*, 4871. (b) Zhang, Q.; Canva, M.; Stegeman, G. *Appl. Phys. Lett.* **1998**, *73*, 912. (c) Cha, M.; Torruellas, W.E.; Stegeman, G.I.; Horstius, W.H.G.; Möhlmann, G.R.; Meth, J. *Appl. Phys. Lett.* **1994**, *65*, 2648. (d) Norwood, R.; Holcomb, D.; So, F. *J. Nonlinear Opt.* **1993**, *6*, 193.

10) For related studies on photo-induced chromophore degradation, see: (a) Shi, Y.; Wang, W.; Lin, W.; Olson, D.J.; Bechtel, J.H. *Appl. Phys. Lett.* **1997**, *70*, 1342. (b) Vydra, J.; Beisinghoff, H.; Tschudi, T.; Eich, M. *Appl. Phys. Lett.* **1996**, *69*, 1035. (c) Dubois, A.; Canva, M.; Brun, A.; Chaput, F.; Boilot, J.-P. *Appl. Opt.* **1996**, *35*, 3193.

11) Albini, A.; Fasani, E.; Pietra, S. *J. Chem. Soc., Perkin Trans. II*, **1982**, 1393.

12) Prêtre, Ph.; Sidick, E.; Wu, L.-M.; Knoesen, A.; Dyer, D.J.; Twieg, R.J. *ACS Symposium Series*, **1997**, *695*, 328.

13) Gordon, P.F.; Gregory, P. *Organic Chemistry in Colour*, Springer-Verlag, Berlin, 1987.

14) Large optical nonlinearities have been achieved using heterocyclic conjugated units and strong heterocyclic acceptors, see: (a) Dirk, C.W.; Katz, H.E.; Schilling, M.L.; King, L.A. *Chem. Mater.* **1990**, *2*, 700. (b) Jen, A.K.-Y.; Rao, V.P.; Wong, K.Y.; Drost, K.J. *J. Chem. Soc., Chem. Commun.* **1993**, 90. (c) Rao, V.P.; Jenn, A.K.-Y.; Cai, Y. *Chem. Commun.* **1996**, 1237. (d) Gilmour, S.; Montgomery, R.A.; Marder, S.R.; Cheng, L.-T.; Jen, A.K.-Y.; Cai, Y.; Perry, J.W.; Dalton, L.R. *Chem. Mater.* **1994**, *6*, 1603. (e) Varanasi, P.R.; Jen, A.K.-Y.; Chandrasekhar, J.; Namboothiri, I.N.N.; Rathna, A. *J. Am. Chem. Soc.* **1996**, *118*, 12443. (f) Marder, S.R.; Cheng, L.-T.; Tiemann, B.G.; Friedli, A.C.; Blanchard-Desce, M.; Perry, J.W.; Skindhøj, J. *Science*, **1994**, *263*, 511. See also: (g) Ikeda, H.; Kawabe, Y.; Sakai, T.; Kawasaki, K. *Chem. Lett.* **1989**, 1803. (h) Ikeda, H.; Sakai, T.; Kawasaki, K. *Chem. Phys. Lett.* **1991**, *179*, 551.

15) For a related study, see: Galvan-Gonzalez, A.; Canva, M.; Stegeman, G.I.; Twieg, R.; Chan, K.P.; Kowalczyk, T.C.; Zhang, X.Q.; Lackritz, H.S.; Marder, S.; Thayumanavan, S. *Opt. Lett.* **2000**, *25*, 332-334..

16) Chromophores **2d** and **5d** have been previously reported, see: (a) Wu, X.M.; Wu, J.Y.; Liu, Y.Q.; Jen, A.K.Y. *J. Am. Chem. Soc.* **1999**, *121*, 472. Chromophores **5e** and **6e** have also been previously reported, see: (b) Jen, A.K.-Y.; Yang, Q.; Marder, S.R.; Dalton, L.R.; Shu C. *F. Mat. Res. Soc. Proc.* **1998**, *488*, 193.

17) It has been previously observed that reduced aggregation could lead to decreased light fastness, see reference 13. However, reduced aggregation is desirable to achieve materials with high chromophores loading. For studies on the relationship between optical nonlinearities and aggregations, see: (a) Dalton, L.R.; Harper, A.W.; Robinson, B.H. *Proc. Nat. Acad. Sci. USA.* **1997**, *94*, 4842. (b) Harper, A.W.; Sun, S.; Dalton, L.R.; Garner, S.M.; Chen, A.; Kalluri, S.; Steier, W.H.; Robinson, B.H. *J. Opt. Soc. Am. B. Opt. Phys.* **1998**, *15*, 329.

18) (a) Driver, M.S.; Hartwig, J.F. *J. Am. Chem. Soc.* **1996**, *118*, 7217. (b) Wolfe, J.P.; Wagaw, S.; Buchwald, S.L. *J. Am. Chem. Soc.* **1996**, *118*, 7215. (c) Hartwig, J.F. *SYNLETT*, **1997**, 329.

19) Thayumanavan, S.; Barlow, S.; Marder, S.R. *Chem. Mater.* **1997**, *9*, 3231.

20) Thayumanavan, S.; Mendez, J.; Marder, S.R. *J. Org. Chem.* **1999**, *64*, 4289.

21) At this point, the chromophore also lost its strong charge transfer absorption in the visible region. ^1H NMR spectra of the chromophore at this juncture afforded broad peaks over the entire spectral region. This type of degradation process also has been observed with other chromophores with phenylisoxazolone acceptor: Levina, G.; Staub, K.; Marder, S.R. unpublished results.

22) It is understood that such an experiment does not rigorously exclude oxygen in solution. However, we suggest that it should have significantly reduced the amount of oxygen in solution and thus should give an idea on the effect of oxygen upon photochemical degradation of these dyes.

23) In fact, the stability of **2a** slightly deteriorates when bubbled with nitrogen as shown in Figure 3. This observed effect is presumed to be negligible within the experimental error.

24) Similarly, the effect of excluding oxygen with **3a** and **4a** was also not significant.

25) Staub, K.; Levina, G.; Barlow, S.; Marder, S.R. Unpublished results.

26) Thermal stabilities of the chromophores chromophores **2d**, **5d**, **5e**, and **6e** have been previously reported, see reference 16.

27) Such a possibility has been proposed in metal catalyzed oxidative decomposition of *N,N*-dialkylanilines, see: Baciocchi, E.; Lanzalunga, O.; Lapi, A.; Manduchi, L. *J. Am. Chem. Soc.* **1998**, *120*, 5783 and references cited therein. Also see reference 13.

28) Such an electron transfer can either be intramolecular or intermolecular.

People supported from this grant:

Seth Marder	P. I.	1996-2000
Peter Bedworth	Post-Doc	1997
J. Kevin Cammack	Post-Doc	1999-2000
S. Thayumanavan	Post-Doc	1997-1999
Katrin Staub	Post-Doc	1997
Galina Levina	Staff	1997
Arjun Mendiratta	Undergraduate Student	1997
Qing Zhang	Post-Doc	1998
Timo Meyer-Friedrichsen	Post-Doc	2000
Wenhui Zhou	Post-Doc	2000

In addition, several people who are not directly receiving funding from this grant but who are performing work in a collaborative manner include:

Marguerite Barzoukas	1997-1998
Mireille Blanchard-Desce	1997
Alain Fort	1997-1998
Alex Jen	1997-1999
Joseph Perry	1996-2000
Galina A. Levina	1998
Stephen Barlow	1998
Hillary Lackritz	1998-1999
Tony Kowalczyk	1998-1999
Katrin Staub	1998
Sundaravel Ananthavel	1999
George Stegeman	1999

Publications

1. P. V. Bedworth, Y.-M. Cai, A. K.-Y. Jen, S. R. Marder, "The Synthesis and Relative Thermal Stabilities of Diphenylamino vs. Piperidinyl Substituted Bithiophene Chromophores for Non-linear Optical Materials." *J. Org. Chem.*, **61**, 2242 (1996)
2. M. Stähelin, M. Alhlein, B. Zysset, S. R. Marder, M. Barzoukas, A. Fort, "Nonlinear Optical Properties of Novel Push-Pull Polyenes for Electro-optics." *J. Op. Soc. Am. B.*, **13**, 2401 (1996)
3. A. K.-Y. Jen, Y. Cai, P. V. Bedworth, S. R. Marder, "Synthesis and Characterization of Highly Efficient and Thermally Stable Diphenylamino-Substituted Thiophene Stilbene Chromophores for Nonlinear Optical Applications." *Adv. Mater.*, **9**, 132 (1997)
4. M. Blanchard-Desce, V. Alain, P. V. Bedworth, S. R. Marder, A. Fort, C. Runser, and M. Barzoukas, "Large Quadratic Hyperpolarizabilities with Donor-acceptor Polyenes Exhibiting Reduced Bond Length Alternation. Correlation between Structure and Hyperpolarizability." *Chem. Eur. J.*, **3**, 1091 (1997)
5. Kippelen, B; Meyers, F.; Peyghambarian, N.; Marder, S.R., "Chromophore Design for Photorefractive Applications." *J. Am. Chem. Soc.*, **119**, 4559 (1997)
6. S. R. Marder, B. Kippelen, A. K.-Y. Jen, N. Peyghambarian "Design and Synthesis of Chromophores and Polymers for Electro-Optics and Photorefractive Applications." *Nature*, **388**, 845 (1997)
7. B. Kippelen, B. L. Volodin, D. D. Steele, E. Hendrickx, D. Sandalphon, Y. Enami, J. L. Maldonado, J. F. Want, A. Golemme, H. Röckel, S. R. Marder, J. B. Javidi, N. Peyghambarian "New Advances in Organic Photorefractive Material Development." *Proc. SPIE*, **3144** (1997)
8. B. Kippelen, B. L .Volodin, O. Savina, D. Sandalphon, H. Röckel, L. Erskine, S. R. Marder, N. Peyghambarian "Photorefractive Polymers with Improved Efficiency." *Proc. CLEO*, (1997)
9. A. K.-Y. Jen, Q. Yang, S. R. Marder, L. Dalton, C.-F. Shu "Recent Progress of Electro-Optic Polymers for Device Applications" in *Electrical, Optical, and Magnetic Properties of Organic Solid-State Materials IV Mat. Res. Soc. Symp.* **488**, 193 (1997)
10. S. Thayumanavan, S. Barlow, S. R. Marder, "Synthesis of Unsymmetrical Triarylamines in One Pot Using Palladium Catalyzed Amination Reactions: Application to Synthesis of Analogs of TPD." *Chem. Mater.* **9**, 3231 (1997)
11. D. D. Steele, B. L. Volodin, O. Savina, B. Kippelen, N. Peyghambarian, H. Röckel, S. R. Marder "Transillumination Imaging Through Scattering Media by Use of Photorefractive Polymers." *Optics Lett.*, **23**, 153 (1998)

12. B. Kippelen, S. R. Marder, E. Hendrickx, J. L. Maldonado, G. Guillemet, B. L. Volodin, D. D. Steele, Y. Enami, D. Sandalphon, Y. J. Yao, J. F. Wang, H. Röckel, L. Erskine, N. Peyghambarian "Infrared Photorefractive Polymers and Their Applications for Imaging." *Science*, **279**, 54 (1998)
13. S. Barlow, M. Day, and S. R. Marder, "The One-electron Oxidation Product of a Metallocenyl-terminated Cyanine," *Acta. Cryst. C***56**, 303-304 (2000)